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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF Project D217

Contract No. DA-18-108-405-CML-777

INHIBITION OF FLASHING OF AEROSOLS

Quarterly Progress Report IV

C. C. Miesse

25 years of research

Unclassified
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ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

DA-18-108-405-CML-777

Quarterly Progress Report No. IV

January 15, 1961 to April 14, 1961

INHIBITION OF FLASHING OF AEROSOLS

C. C. Miesse

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This fourth Quarterly Progress Report summarizes the work performed during the past twelve (12) months, with special emphasis on the fourth quarter, from January 15, 1961 to April 14, 1961, under Contract No. DA-18-108-405-CML-777, on the study of "Inhibition of Flashing of Aerosols", for the Physical Chemistry Division of the Army Chemical Center, Edgewood, Maryland.

The following personnel have contributed to this project during the fourth quarter: C. C. Miesse, S. Noreikis, and D. Werle.

Data are recorded in Armour Research Foundation Logbook D-1317.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

C C Miesse

C. C. Miesse, Principal Investigator

F. Iwatsuki

F. Iwatsuki, Supervisor

APPROVED:

J. Pinsky

J. Pinsky, Assistant Director of
Fluid Dynamics and Propulsion Research

CCM/aa

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I. ABSTRACT

The fourth Quarterly Progress Report summarizes the work performed on the project during the past twelve-month period, with particular emphasis on the fourth Quarter's activities. Experimental work during the year included design, construction and operation of the aerosol generator and combustion tube; development of a photographic technique for determination of the drop size distribution; and determination of the variation of flammability limits with operating conditions. This latter phase, which was initiated during the fourth Quarter, indicated that the lower limit of flammability increases with the Sauter Mean Diameter (SMD) of the aerosol. Theoretical work during the year included analysis of both stationary and falling aerosols. The former analysis predicted that limit concentrations would be independent of drop size. The latter analysis indicated a negligible variation of concentration with vertical distance; and consideration of the theoretical transverse variation predicted the experimentally observed increase of lower limit concentration with droplet diameter.

II. INTRODUCTION

This project under Contract DA-18-108-405-CML-777 was initiated on April 15, 1960, by the Army Chemical Center, to investigate fundamental behavior in the flashing of flammable liquid aerosols so that means of prevention or inhibition of the flashing may be revealed. The variables to be investigated include mass concentration, drop size, liquid volatility, ignition source, and, if possible, pressure and temperature.

In the second phase of this study, flame inhibiting additives will be investigated.

During the first twelve months of the project, techniques for generating, igniting and characterising aerosols of various concentrations and mean drop sizes were developed and an analytical theory for determining the variation of critical concentration with drop size in a descending monodisperse aerosol, evenly spaced, was derived. Initial experimental variations of limit concentrations with Sauter Mean Diameter showed excellent qualitative agreement with theoretically derived limit curves. During the course of the project, a direct photographic method for determining drop size distributions was developed, although the need for extensive improvement of the technique led to a recent decision to utilize the familiar coated slide technique in future endeavors.

III. EXPERIMENTAL INVESTIGATION

Experimental activity during the year included the design, construction and operation of the aerosol generator and combustion tube; development of a direct photographic technique for determination of drop size distribution in the descending aerosol; and the determination of the variation of flame propagation characteristics with operating conditions.

During the first Quarter, various methods for providing monodisperse aerosols were investigated, and it was determined that the best type for the purposes of the present project is a modified Sinclair-LaMer generator, used by Burgoyne and Cohen (1) and further modified by Rapaport and Weinstock (2). Whereas Rapaport used a nebulizer to spray high boiling liquids into an evaporator, a two-fluid spray nozzle was installed in the present apparatus to permit the

attainment of higher aerosol concentrations. As indicated by Fig. 1, the vaporizer consists of a 2-1/2 inch diameter aluminum block, 5-1/2 inches long, maintained at a temperature close to the boiling point by means of a thermostatically controlled heating element. Condensation takes place in a 2-inch I.D. inverted glass chimney directly below the vaporizer. At first, a 4-foot long chimney was tried, but cooling to room temperature was observed to occur after but about 8 inches of travel and the long chimney length served only to render the aerosol less homogeneous through growth by turbulent accretion. Therefore, the cooling chimney was shortened to 12-1/2 inches.

An aerosol attenuator or valve was made to give some control over mass concentration that would be independent of the generator controls. A 1/4-inch thick perforated metal plate with 15/64-inch diameter holes space 1/4-inch apart (43.1 per cent open area) rotated so that the projected area can be varied continuously between 0 and 43.1 per cent open area. Qualitative operation of this valve has shown that concentrations can be varied at a given generator setting to above or below the lower explosive limit simply by rotation of the perforated plate.

During the second Quarter, the apparatus was modified by installation of more desirable components, substitution of more precise flow control instrumentation, and replacement of the aerosol valve-type attenuator by wire mesh in order to minimize flow disturbances. A typical droplet configuration on the magnesium-coated slide is shown in Fig. 2. From this figure it is apparent that the predominance of the faster-falling larger droplets tends to bias the drop size distribution in favor of the larger sizes.

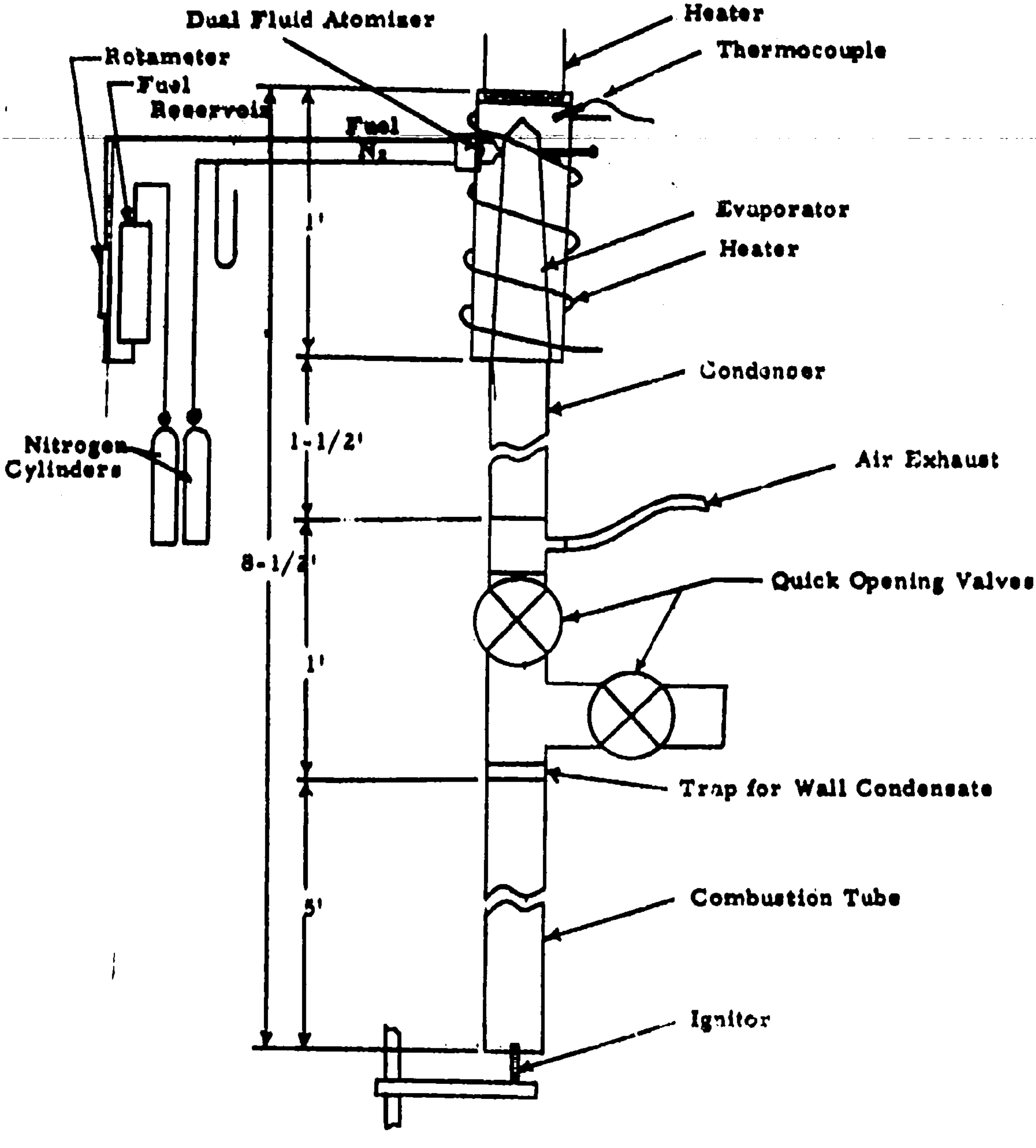


Fig. 1 SCHEMATIC DIAGRAM OF COMBUSTION APPARATUS

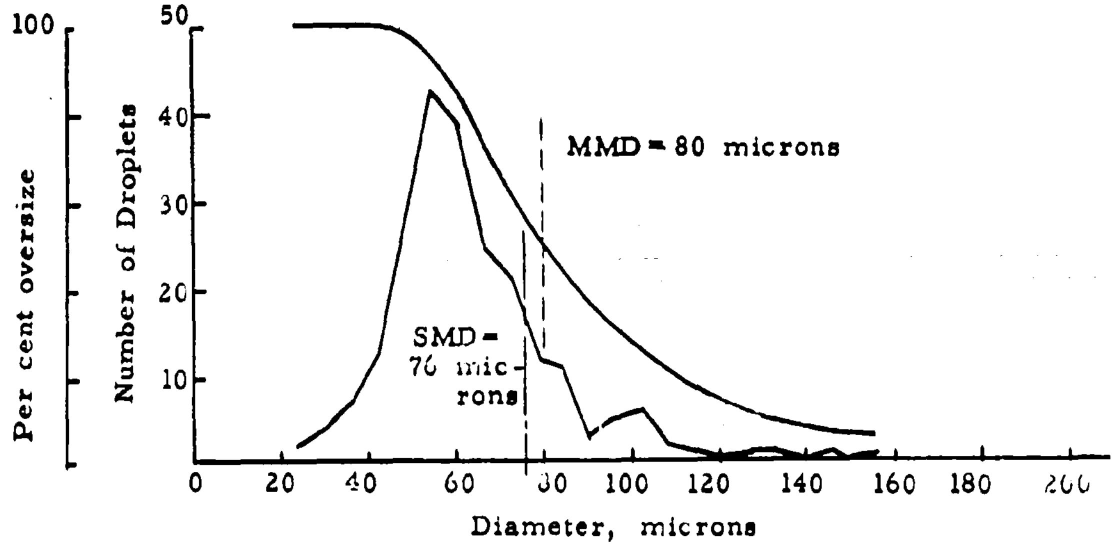
Fig. 2 TYPICAL DROPLET CONFIGURATION ON MAGNESIUM-COATED SLIDE

In order to eliminate this apparent bias, a photographic technique was developed during the third Quarter, whereby the droplets falling within the narrow focal field of camera are illuminated by two GE photospot lights mounted behind the aerosol sheet, at 45 degrees to the focal axis. From the typical photograph shown in Fig. 3, it is apparent that a larger number of droplets are included in the sample, which provides a representative consist in that more of the smaller droplets are included. Typical drop size distributions obtained by this technique are shown in Fig. 4, and the resultant variation of Sauter Mean Diameter[1] with operating conditions is shown in Fig. 5. For comparison purposes, a corresponding variation obtained by the coated-slide technique is included, thus demonstrating the influence of the larger number of small droplets which can be observed by direct photography. The proximity of the several curves obtained from direct photography indicates the minor effect of variation in the flow rate of the atomizing nitrogen.

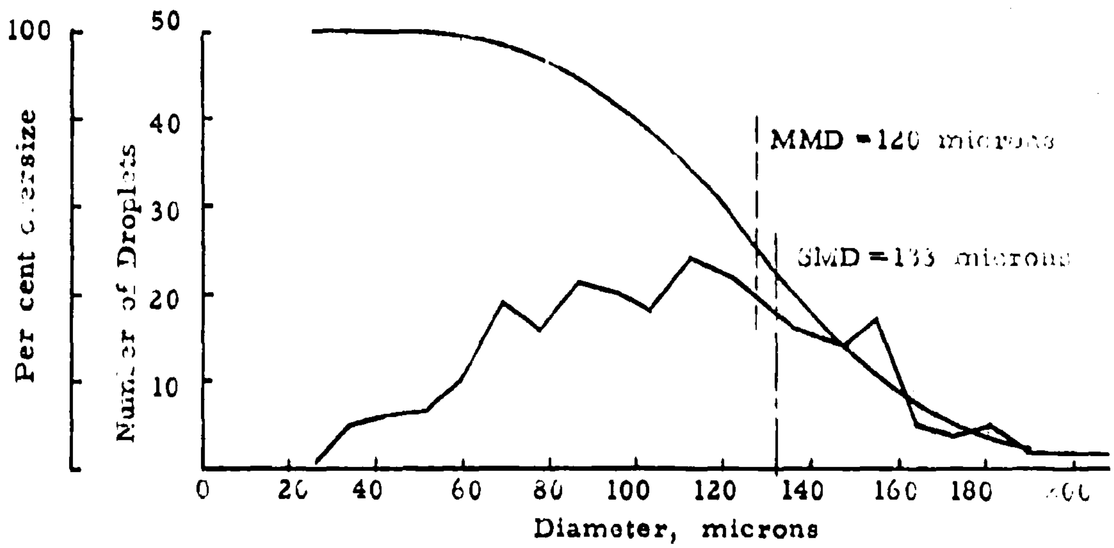
The final Quarter witnessed the experimental determination of the variation of flammability limits with operating conditions. For excessively lean mixtures, no flame was observed, or initial ignition flames failed to propagate. At higher concentrations, an umbrella-shaped flame was observed to travel up the combustion tube, as depicted by Fig. 6. From this figure it is apparent that the flame propagates from one vapor source (droplet) to the next. At higher concentrations, a type of flashback was observed at the upper terminus of the combustion tube, and

[1] $SMD = \frac{\sum n d^3}{\sum n d^2}$ = the diameter of droplet which has the specific surface equivalent to the aggregate of droplets in the spray

Fig. 3 TYPICAL PHOTOGRAPH OF DESCENDING AEROSOL

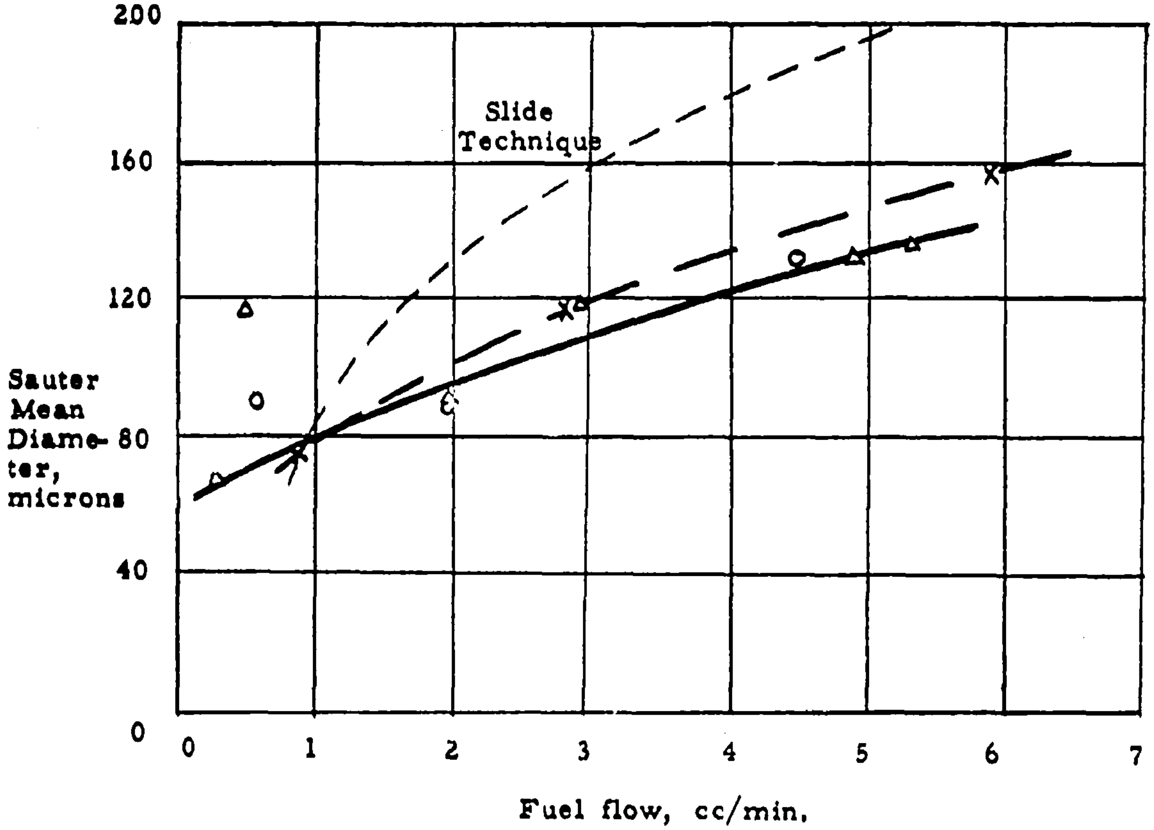


(a) Nitrogen Flow = 2 liters/min., Fuel flow = 0.9 cc/min.



(b) Nitrogen Flow = 3 liters/min., Fuel flow = 4.5 cc/min.

Fig. 4 TYPICAL DROP SIZE DISTRIBUTIONS



Symbol	Nitrogen Flow
△ —— △	1.0 liters/min.
X — — X	2.0
O —— O	3.0

Fig. 5 VARIATION OF SAUTER MEAN DIAMETER WITH OPERATING CONDITIONS

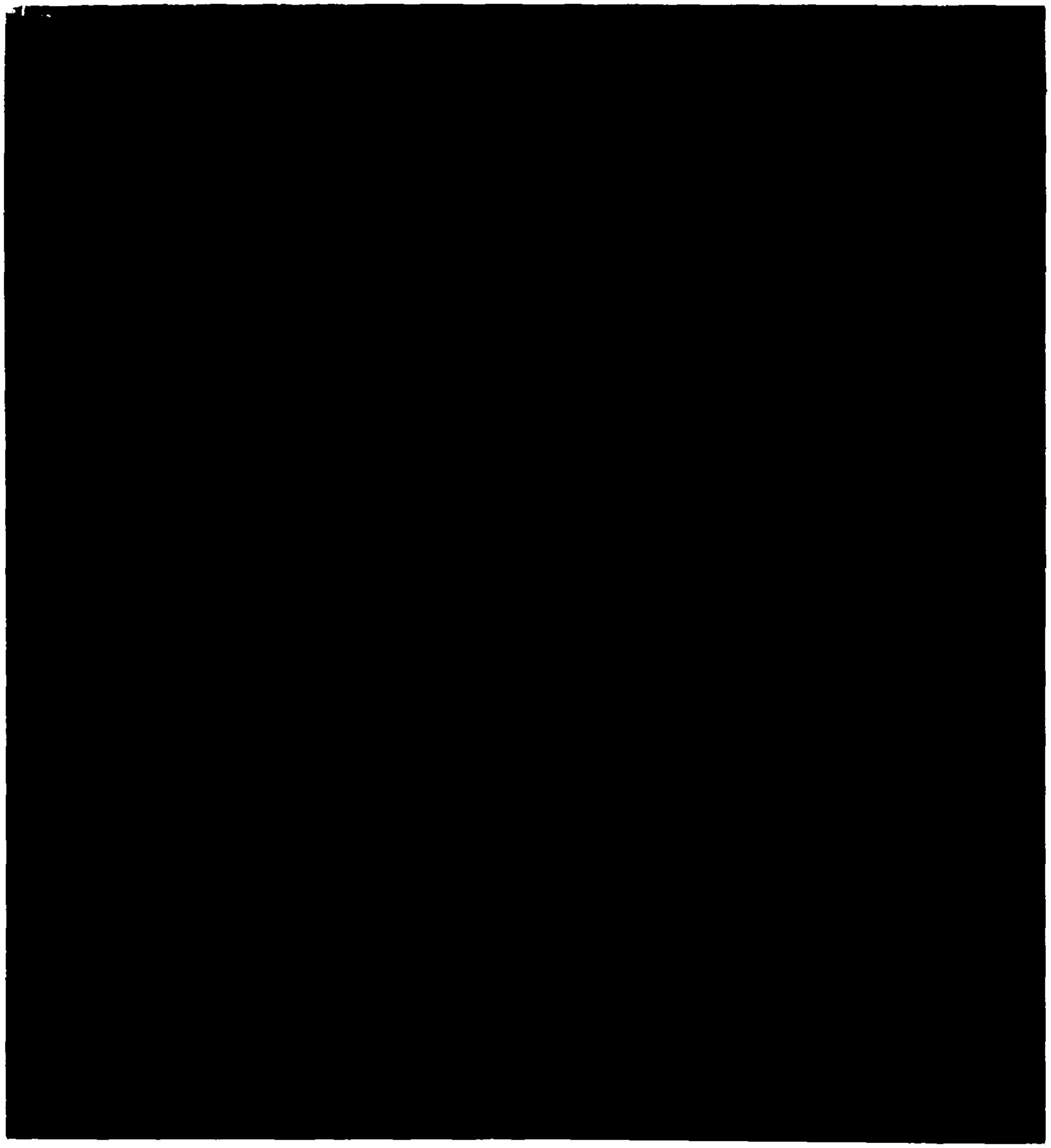


Fig. 6 TYPICAL PHOTOGRAPH OF DROP-TO-DROP FLAME PROPAGATION

under some few no-oxygen conditions, the absence of flammability indicated that the rich limit had been attained. The several regions of flammability are shown in Fig. 7a, while the resultant variation of concentration[1] with SMD at the limiting conditions is shown in Fig. 7b. From this latter figure, it appears that minimum concentration required for flame propagation increases with SMD, as noted previously by Anson (3) in his studies with kerosene sprays.

IV. THEORETICAL ANALYSES

Theoretical derivations performed during the past twelve months include the analyses of fuel vapor concentrations in stationary and descending aerosols. In the former case, the minimum droplet spacing for flame propagation in a monodisperse aerosol was found to vary directly with droplet diameter;hence for equally spaced droplets, the lower limit of flammability is independent of drop size. In the latter case, the concentration was found to be essentially independent of vertical distance and the transverse variation predicted an increase in the lower flammability limit with drop size, for a monodisperse equally-spaced aerosol.

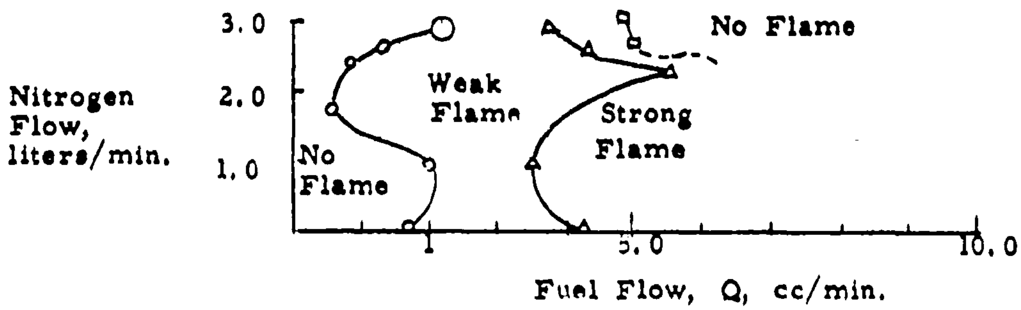
The dif..rential equation for the stationary case is expressed in spherical coordinates, where spherical symmetry is assumed:

---

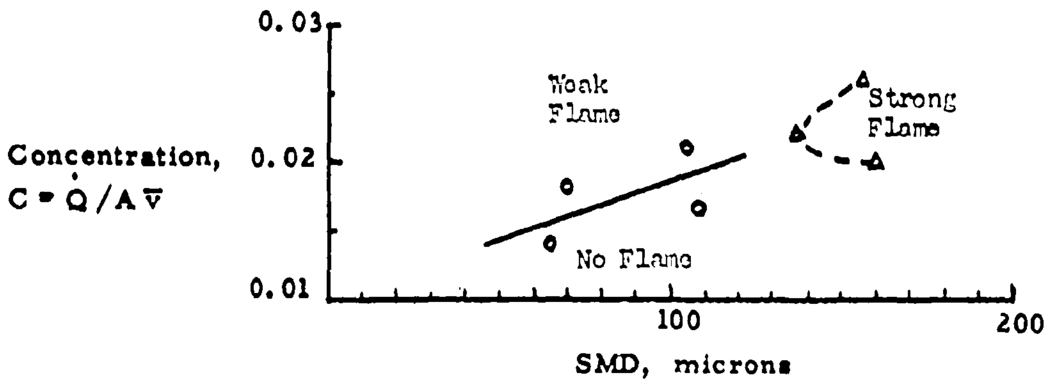
[1] The concentration (C) of the aerosol, being defined as quantity (cc) of liquid per unit volume, in space, was determined by the equation

$$C = \frac{\dot{Q} \Delta t}{A \bar{v} \Delta t}$$

where $\dot{Q}$ is the volume rate of aerosol generation, A is the combustion tube's cross-sectional area, and $\bar{v}$ is the terminal velocity of the droplets. The numerator thus represents the quantity of liquid supplied in time Δt, while the denominator represents the corresponding volume which is occupied by the aerosol in the same time interval.



(a)



(b)

Fig. 7 VARIATION OF FLAMMABILITY LIMITS WITH OPERATING CONDITIONS: NO AIR FLOW

$$\frac{\partial C}{\partial t} = \alpha \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \qquad (1)$$

where α is the diffusion coefficient and r is the radial distance. By considering each drop to be a spherical vapor source, a relation between the independent variables can be established (cf. Burke and Schuman [4] and Miesse [5]) in terms of the diffusing vapor velocity (v') and the mass evaporation rate (M)

$$\frac{dr}{dt} = v' = \frac{M}{4 \pi \rho r^2} \qquad (2)$$

Furthermore, the mass evaporation rate was shown by Ranz and Marshall (6) to vary with the droplet diameter (D):

$$M = k D \qquad (3)$$

Substitution of Equations 2 and 3 into Equation 1 resulted in a second order equation for C in terms of r which could be integrated directly. Substitution of the appropriate boundary conditions revealed the direct variation of minimum spacing with droplet diameter. Governing parameters included the stoichiometric mixture ratio, fuel and oxidant concentrations, and the dimensionless group $k/\rho_f \alpha$, which represents the ratio of evaporation rate (supply) to diffusion rate (dissipation) . As could be expected, higher evaporation rates result in larger values for the maximum separation distance.

In the second analysis, the mass concentration equation was expressed in cylindrical coordinates to correspond with the physical model depicted in Fig. 8:

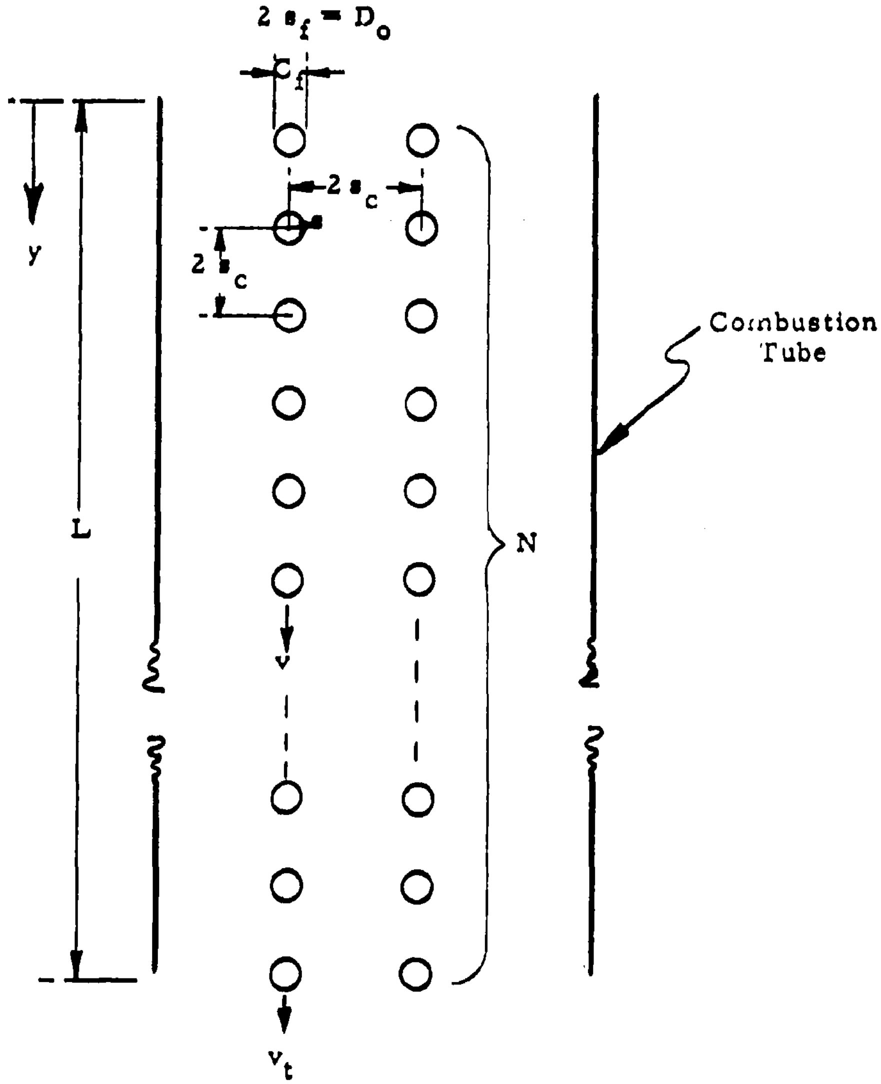


Fig. 8 SCHEMATIC DIAGRAM OF THEORETICAL MODEL FOR FALLING AEROSOL

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial y} = \alpha \left[\frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial s^2} + \frac{1}{s} \quad \frac{\partial C}{\partial s} \right] \tag{4}$$

where v is the velocity of the falling droplets, and y and s are the vertical and transverse (radial) coordinates, respectively. Substitution of Equation 2, Stokes' Law

$$\frac{dv}{dt} = g - \frac{Kv}{D_o^2} = a \tag{5}$$

and the assumed product function

$$C\ (s, v) = S(s) \quad \cdot \quad V(v) \tag{6}$$

into Equation 4 yields the following simultaneous ordinary differential equations for S and V:

$$S'' - \frac{1}{s} S' - \frac{b}{s^2} \quad S' \tag{7}$$

and

$$av\ \ddot{V} - (g + \frac{v^3}{\alpha}) \quad \dot{V} = 0 \tag{8}$$

where $b = M/4\pi\rho\alpha$ and the primes and dots represent differentiation with respect to s and v, respectively. Equation 7 can be integrated directly to yield the solution

$$S = \frac{C_f \quad E\,i\,(-b/s)}{E\,i\,(-b/s_f)} \tag{9}$$

where $E\,i\,(x)$ is the exponential integral (7), C_f is the saturation fuel concentration at the droplet surface ($s = s_f$). Typical transverse

variations of concentration are shown in Fig. 9. Although Equation 8 could be integrated only once, in closed form, substitution of representative values for the governing parameters into the resultant equation for $\dot{V}$ revealed that $\dot{V} \approx 0$ except for a negligible distance ($\leqslant$ 1 mm) from the lower terminus of the combustion tube. Hence valid approximations could be introduced which resulted in the following expression for the V component of concentration:

$$\frac{V}{N} = 1 - \left(\frac{q}{1 - z} \right)^{\phi} \tag{10}$$

where N is the total number of droplets in a single vertical stream,

$$\left.\begin{aligned} z &= v/\bar{v} \\ q &= 1 - v_t/\bar{v} \\ \bar{v} &= g\, D_o^{\,2}/K \qquad \text{(terminal velocity)} \\ \phi &= \bar{v}^3/g\,\alpha \end{aligned}\right\} \tag{11}$$

and v_t is the droplet velocity at the lower end of the combustion tube. Since $v_t \approx \bar{v}$, it is readily apparent that $V/N \approx 1$ for most of the length of the combustion tube, as shown in Fig. 10. Hence, from Equations 6 and 9 the concentration distribution can be adequately represented by the equation

$$C = \frac{N\, C_f\ Ei\,(-b/s)}{Ei\,(-b/s_f)} \tag{12}$$

for all but an infinitesimal distance from the lower terminus.

Project activity during the fourth Quarter consisted of a determination of the variation of the liquid concentration ($\bar{C}$) at the lower limit of flammability, with drop size in a monodisperse equally-spaced

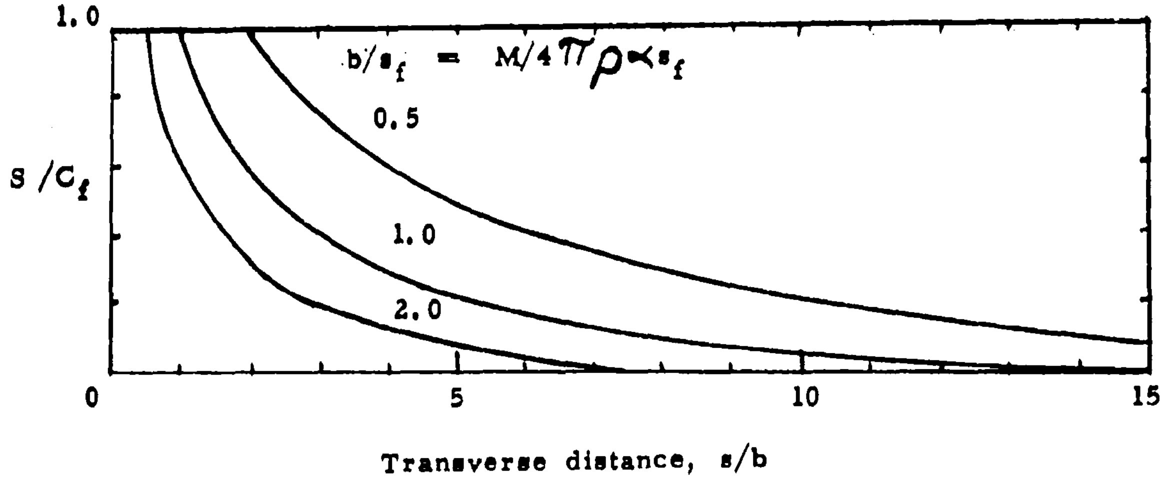


Fig 9 TRANSVERSE VARIATION OF VAPOR CONCENTRATION FOR VARIOUS VAPORIZATION RATES (M)

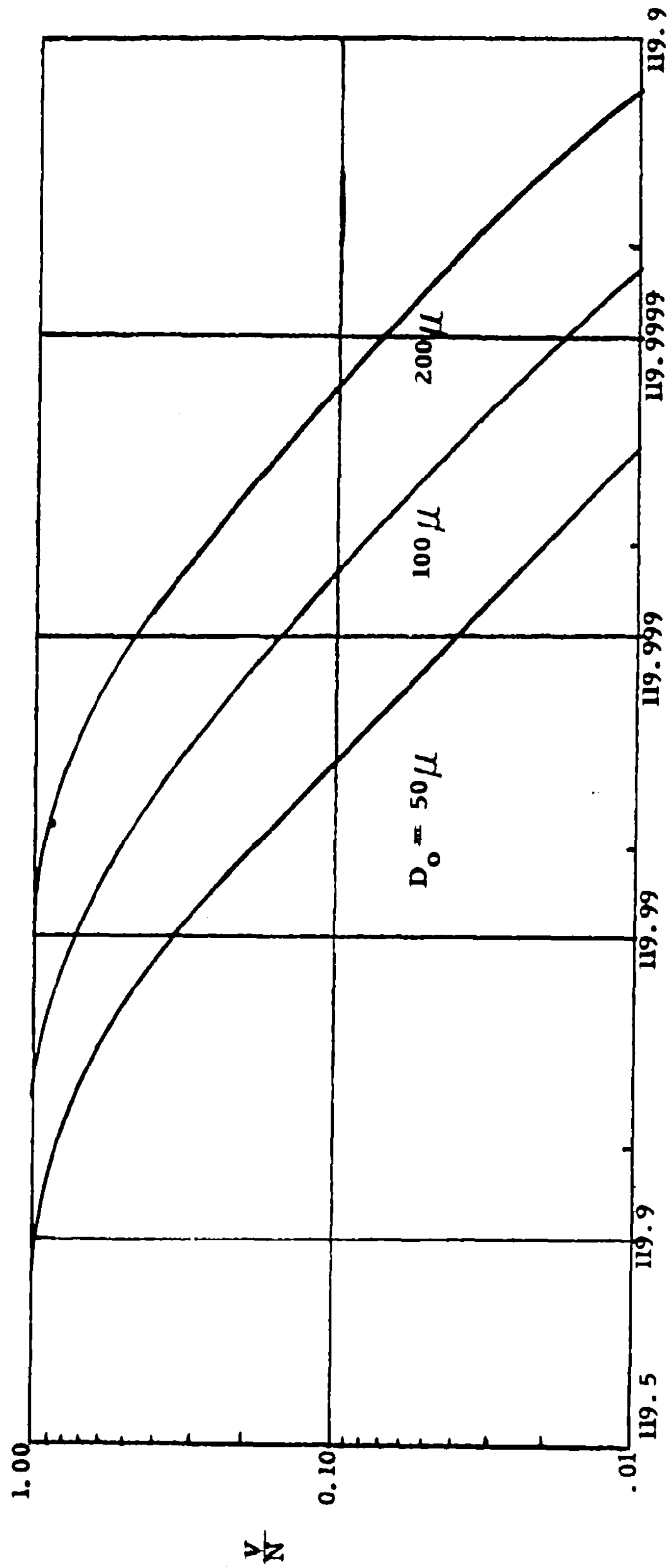


Fig.10 VERTICAL VARIATION OF VAPOR CONCENTRATION FOR VARIOUS DROPLET DIAMETERS

aerosol. It is first postulated that the critical droplet spacing (s_c) will be that for which $C = C_{min}/2$, where C_{min} is the minimum concentration for flame propagation. From Equations 2 and 9 and the definition of b, it is apparent that, for a given simulant,

$$N\ Ei\,(-s_f/s_c) = \frac{C_{min}}{2\,C_f}\ Ei\,(-b/s_f)$$

$$= \frac{C_{min}}{2\,C_f}\ Ei\,(-k/4\pi\rho\alpha) = \text{constant} \qquad (13)$$

Hence, the right side of Equation 13 can be determined from a knowledge of the simulant properties, and the variation of N with s_f/s_c can be calculated. For equal droplet spacing (vertical as well as transverse),

$$s_c = L/2N \qquad (14)$$

where L is the length of the combustion tube. Similarly, the concentration of liquid simulant ($\bar{C}$) can be represented by the equation

$$\bar{C} = (\tfrac{4}{3}\ \pi s_f^3)/(8\ s_c^3) = \frac{\pi}{6}\,(s_f/s_c)^3 \qquad (15)$$

Thus, from a knowledge of b/s_f, the variation of N with s_f/s_c can be determined; Equation 15 then permits the determination of the variation of $\bar{C}$ with N; and Equations 13 and 14 facilitate a one-to-one correspondence between N and the appropriate value of s_f.

Qualitative indication of the predicted variation of $\bar{C}$ with $D_o = 2\ s_f$ is shown in Fig. 11, which resulted from the following assumed values of the parameters:

L = 120 cm.

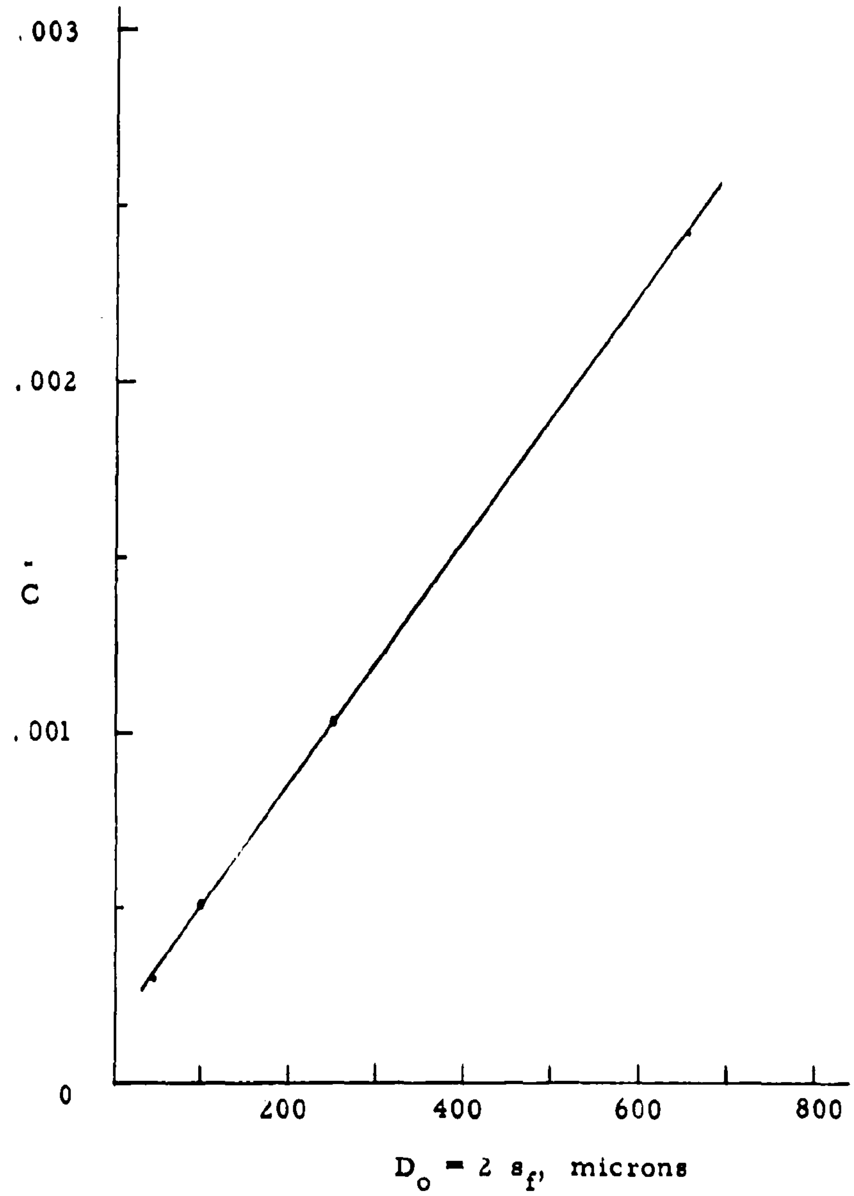


Fig. 11 THEORETICAL VARIATION OF LIQUID CONCENTRATION WITH DROPLET DIAMETER AT LOWER LIMIT OF FLAMMABILITY

$$b/s_f = 1.0$$

$$C_{min}/C_f = 240$$

Inspection of this figure reveals that the critical concentration (at the lower limit of flammability) increases almost linearly with drop size, thus providing qualitative confirmation of the trend noted in the experimental curve presented in Fig. 7b.

V. CONCLUSIONS

As a result of the first year's investigation of the flashing of Dibutyl Phthalate aerosols, the following conclusions can be drawn:

1. The lower limit of flammability is increased by an increase in drop size (experimentally and theoretically), a decrease in volatility, or an increase in mass diffusion rate (theoretically).
2. Mean droplet size increases with fuel flow rate, but is relatively unaffected by the flow rate of atomizing nitrogen (experimental).
3. In the absence of a purging air flow, upper limits of flammability can be attained in the present apparatus, probably due to the high proportion of atomizing nitrogen in the atmosphere surrounding the simulant aerosol (experimental).
4. The difficulties and uncertainties involved in the photographic technique for measuring drop size distribution recommend the utilization of the coated-slide technique, in order to obviate the need for additional

effort required to perfect the photographic technique.

VI. FUTURE WORK

Due to the errors involved in estimating the size of out-of-focus droplets, it is planned to make future determinations of drop size distributions using the magnesium slide technique, in which corrections can be made to account for the bias in favor of the faster-falling larger droplets.

Inasmuch as the thermal aerosol generator operating data previously obtained is incomplete and open to question, it appears advisable to repeat some of the experiments. However, to conserve time, flammability tests will be conducted concurrently with the generator performance tests so that only those generator operating parameters in the region of flammability need be investigated in detail. The flammability tests will also be conducted with one or more other high boiling liquids, one of which will be bis (2-ethyl hexyl) hydrogen phosphite. After flammability limits versus drop size and concentration have been determined for DBP and B2EHHP aerosols produced by the thermal generator, gaseous inhibitors will be metered into the combustion air and the effect of inhibitor concentration on the flammability limits will be determined.

The design and construction of a large drop (>200 microns diameter) aerosol generator will be completed and the flammability and inhibition studies will be extended for the large drop aerosols in much the same manner as described above. In addition to the use of gaseous inhibitors, liquid or solid inhibitors dissolved or suspended in the DBP and B2EHHP will also be evaluated. The large drop aerosol will

present a serious mass sampling problem due to the high settling velocities and techniques will be developed for this, i.e., possible chemical analysis of the combustion products after ignition.

The theoretical analysis of diffusion from a descending aerosol will be utilized to determine concentration limits of flammability in a monodisperse equally-spaced aerosol, and will be extended to the case of non-uniform consists of non-homogeneous spatial distribution. The effects of temperature and pressure will be investigated, and a theoretical analysis of the effects of inhibitors will be derived. Theoretical concepts will be applied to the correlation and explanation of experimental data.

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